

Electrode Kinetics of the Redox Reaction of Tris(2,2'-bipyridine)nickel Complexes in an Ionic Liquid

Yasushi Katayama*, Yuichi Toshimitsu, Takashi Miura

Keio University, Department of Applied Chemistry, Faculty of Science and Technology, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan



ARTICLE INFO

Article history:

Received 2 September 2013

Received in revised form

26 November 2013

Accepted 13 December 2013

Available online 4 January 2014

Keywords:

Ionic liquid

Tris(2,2'-bipyridine)nickel complex

AC impedance

Electrode kinetics

ABSTRACT

Electrode reaction of tris(2,2'-bipyridine)nickel complexes, $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$, was investigated in an aprotic ionic liquid, 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMPTFSA) using AC impedance spectroscopy. The formal potential of $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ was 1.37 V vs. ferrocene/ferrocenium at 25 °C. The diffusion coefficients of $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$ at 25 °C were 4.2 and $7.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, respectively, which are close to those of $[\text{M}(\text{bpy})_3]^{3+}$ and $[\text{M}(\text{bpy})_3]^{2+}$ (M = Ru and Fe) due to the similarity in the charge densities. The activation energies for the diffusion coefficients were close to that for the viscosity of the ionic liquid, indicating the viscosity is a major factor that determines the diffusion of the complexes. The rate constant of $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ was $8.3 \times 10^{-6} \text{ cm s}^{-1}$, which is smaller by two orders of magnitude than those for $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ and $[\text{Fe}(\text{bpy})_3]^{3+/2+}$, reflecting the slow electron transfer caused by participation of the anti-bonding molecular orbital in the redox reaction. The apparent activation energy for the rate constant of $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ is considered determined not only by the activation energy for the viscosity but also by the reorganization energy, of which the inner component is larger than those in $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ and $[\text{Fe}(\text{bpy})_3]^{3+/2+}$.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Aprotic ionic liquids have been expected to be promising electrolytes alternative to conventional organic electrolytes due to intrinsic ionic conductivity, negligible volatility and wide electrochemical potential window[1]. Ionic liquids can be liquid at low temperature since they are composed of the bulky ions, of which the electrostatic interaction is weak. On the other hand, bulkiness of the constituent ions often leads to high viscosity and slow dynamics, which are expected to affect electrode kinetics of electroactive species in ionic liquids. We have already studied the electrode reactions of tris(2,2'-bipyridine) complexes of some transition metals ($[\text{M}(\text{bpy})_3]^{n+}$) in the ionic liquids consisting of bis(trifluoromethylsulfonyl)amide (TFSA[−])[2–4]. It has been found that the diffusion of the charged species is affected not only by the viscosity of the ionic liquids but also by the coulombic interaction of the diffusing species with the ions composing the ionic liquids. Although the redox reactions of the bpy complexes are classified into an outer-sphere electron transfer reaction, the rate constant has been found to depend strongly on the viscosity, which is mainly related to the frequency (or pre-exponential) factor of Arrhenius-type expression of the rate constant. According to

Marcus theory, the rate constant is related to the reorganization energy, which is divided into inner and outer components[5]. The inner component of the reorganization energy is mainly related to the change of bond length between the center atom and the ligands. The outer component of the reorganization energy in polar solvents is given by dielectric interaction between the complex and the solvent molecules. In case of ionic liquids, however, the outer component of the reorganization energy is expected to be replaced with the coulombic and inter-molecular interactions between the complex and the ions composing the ionic liquids. On the other hand, the inner component is considered independent of the physical properties of reaction media. In the present study, the influence of the inner component of the reorganization energy on the electrode kinetics of the bpy complexes was investigated in an TFSA[−]-based ionic liquid, BMPTFSA (BMP⁺ = 1-butyl-1-methylpyrrolidinium).

The redox reactions of metal complexes are expected to be applicable for the redox flow batteries using aprotic ionic liquids[6–10]. Since the electrochemical potential window of aprotic ionic liquids is often wider than that of aqueous solution, it may be possible to realize the larger cell voltage, which leads to increase the energy density. The bpy complexes are promising electroactive species for redox flow batteries since they can take multiple valence states including the electron transfer to/from the bpy ligands. Although some bpy complexes are unstable in conventional organic solvents[11], there is a possibility that such bpy complexes are stabilized in the ionic liquid based on TFSA[−], of which the

* Corresponding author.

E-mail address: katayama@applc.keio.ac.jp (Y. Katayama).

donor ability is much lower than those of conventional organic solvents[8]. In this study, the redox reaction between divalent and trivalent tris(bpy) nickel complexes was investigated in BMPTFSA.

2. Experimental

BMPBr was prepared by the reaction of 1-methylpyrrolidine (Tokyo Chemical Industry, 98%) with butyl bromide (Tokyo Chemical Industry, 98%) in acetonitrile (Junsei Chemical, 99.5%) at ambient temperature. Then, BMPBr was purified by recrystallization from its acetonitrile solution with ethyl acetate (Junsei Chemical, 99.5%) for three times and finally dried under vacuum at 120 °C for 24 hours[12]. BMPTFSA was prepared by the metathesis reaction between BMPBr and LiTFSA (Kanto Chemical, 99.9%) in deionized water, then extracted into dichloromethane (Junsei Chemical, 99.5%), separated by evaporation and finally dried under vacuum at 120 °C for 24 hours. The water content of BMPTFSA was found to be below 10 ppm by Karl Fischer titration (Metrohm, 831KF Coulometer). Ni(TFSA)₂ was prepared by reacting NiCO₃·Ni(OH)₂·4H₂O (Kanto Chemical) with HTFSA (Morita Chemical Industry, 99%) aqueous solution at 80 °C, filtered to separate unreacted starting materials and finally dried under vacuum at 160 °C for 24 hours[13]. [Ni(bpy)₃]²⁺ was introduced by adding Ni(TFSA)₂ and bpy (Wako Pure Chemical Industries, 99.5%) at a molar ratio of 1: 3 into BMPTFSA. All the hygroscopic reagents were stored and handled in an argon filled glove box with a continuous gas purification apparatus (Miwa MFG, DBO-1KP-K01). The concentrations of water and oxygen were kept below 800 ppb and 1 ppm, respectively.

Electrochemical measurements were conducted with an air-tight three-electrode cell using a potentiostat/galvanostat (Hokuto Denko, HABF-501). A platinum disk (3 mmφ) was used as a working electrode. The active area of the platinum disk was mechanically polished and washed with deionized water before use. A platinum wire was used as a counter electrode. A silver wire immersed in EMITFSA (EMI⁺ = 1-ethyl-3-methylimidazolium, Kanto Chemical) containing 0.1 M AgCF₃SO₃ (Aldrich, 99%) was used as a reference electrode. All the potentials in this paper were given against this reference electrode denoted as Ag/Ag(I). The potential of this reference electrode was +0.44 V vs. ferrocene (Fc)/ferrocenium (Fc⁺) couple in BMPTFSA at 25 °C[9]. The temperature dependence of the potential of the reference electrode is 0.55 ± 0.02 mV K⁻¹[14]. Bulk electrolysis was conducted in order to prepare the ionic liquid containing both [Ni(bpy)₃]²⁺ and [Ni(bpy)₃]³⁺ at the same concentration. A two-compartment cell separated by a glass filter was used for the bulk electrolysis, in which carbon felt was used as the cathode and anode. AC impedance measurements were carried out with PARSTAT 2273 (Princeton Applied Research). The AC amplitude was ±10 mV rms. The frequency range was from 1 Hz to 10 kHz. The influence of the reference electrode on the impedance measurements was assumed to be negligible in this study. The viscosity of the ionic liquid was measured by a vibronic viscometer (Yamaichi Electric, VM-1G-L). The ultra-violet and visible (UV-VIS) absorption spectrum of the ionic liquid was taken by UV-VIS spectrometer (JASCO, V-530) with an air-tight quartz cell (light path length: 1 mm).

3. Results and Discussion

Ni(TFSA)₂ dissolved in BMPTFSA to give a pale green ionic liquid, indicating Ni²⁺ is octahedrally coordinated by six oxygen atoms of TFSA⁻ anions[13]. When bpy was added to the ionic liquid at the molar ratio of Ni²⁺: bpy = 1: 3, the color of the ionic liquid turned to pale pink. The UV-VIS spectrum of the ionic liquid gave two absorption bands at 521 and 787 nm, which were close to those observed

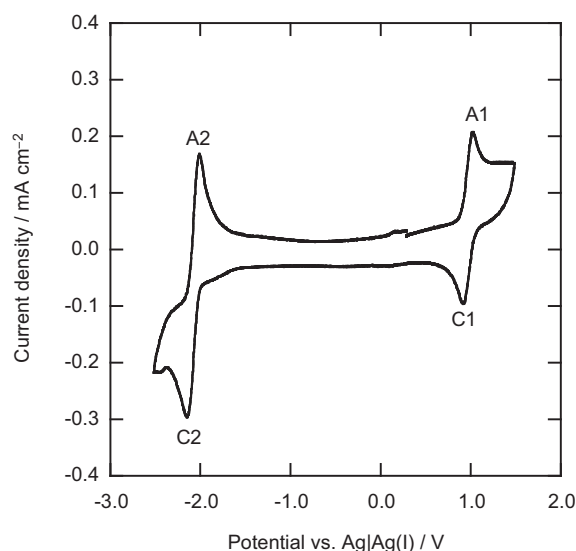
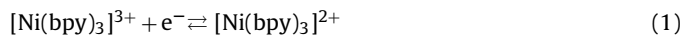


Fig. 1. Cyclic voltammogram of a Pt electrode in BMPTFSA containing 40 mM [Ni(bpy)₃]²⁺ at 25 °C. Scan rate: 10 mV s⁻¹.

in the aqueous solution containing [Ni(bpy)₃](ClO₄)₂, 521 and 790 nm, respectively[15]. Thus, it was confirmed that [Ni(bpy)₃]²⁺ was introduced in BMPTFSA. Fig. 1 shows the cyclic voltammogram of a platinum electrode in BMPTFSA containing 40 mM [Ni(bpy)₃]²⁺. Two pairs of anodic and cathodic current peaks were observed around +1.0 (A1/C1) and -2.1 (A2/C2) V. It has been reported that [Ni(bpy)₃]²⁺ can be oxidized to [Ni(bpy)₃]³⁺ in liquid SO₂[16] and acetonitrile[15,17]. Thus, the redox current peaks observed at the positive potential region can be assigned to the following reaction.



The cathodic current peak at -2.1 V is considered corresponding to the two-electron transfer reduction of [Ni(bpy)₃]²⁺ to Ni(bpy)₃, which have been reported in acetonitrile [17,18] and propylene carbonate [6].



In case of acetonitrile, further reduction of Ni(bpy)₃ and/or liberation of bpy from the complexes have been reported to occur[17,18], probably due to stronger donor ability of acetonitrile as compared with that of BMPTFSA[8]. On the other hand, [Ni(bpy)₃]²⁺ is also reported to be reduced to [Ni(bpy)₃]⁺ as is the case for [M(bpy)₃]²⁺ (M = Fe and Ru)[19]. In this study, only the redox reaction between [Ni(bpy)₃]³⁺ and [Ni(bpy)₃]²⁺ was investigated in detail.

Fig. 2 shows the cyclic voltammograms of a platinum electrode in BMPTFSA containing 40 mM [Ni(bpy)₃]²⁺ at various scan rates within the potential range including the redox reaction between [Ni(bpy)₃]³⁺ and [Ni(bpy)₃]²⁺. The anodic peak potential shifted to more positive side with an increase in the scan rate. In addition, the separation between the half peak potential and the peak potential at 10 mV s⁻¹ was 83 mV, which was larger than the theoretical value for a one-electron transfer reversible reaction (56.5 mV) at 25 °C[20]. Thus, the electrode reaction can be regarded as quasi- or irreversible. Bulk electrolysis was conducted in order to prepare the ionic liquid containing both [Ni(bpy)₃]³⁺ and [Ni(bpy)₃]²⁺ at the same concentration. Fig. 3 shows the open circuit potential of a platinum electrode during the bulk electrolysis on the logarithm of the concentration ratio of [Ni(bpy)₃]³⁺ to [Ni(bpy)₃]²⁺. The concentration was calculated assuming the current efficiency to be 100%. The plots could be fitted to a straight line with a slope of 60 mV, which was consistent with the theoretical value for a one-electron

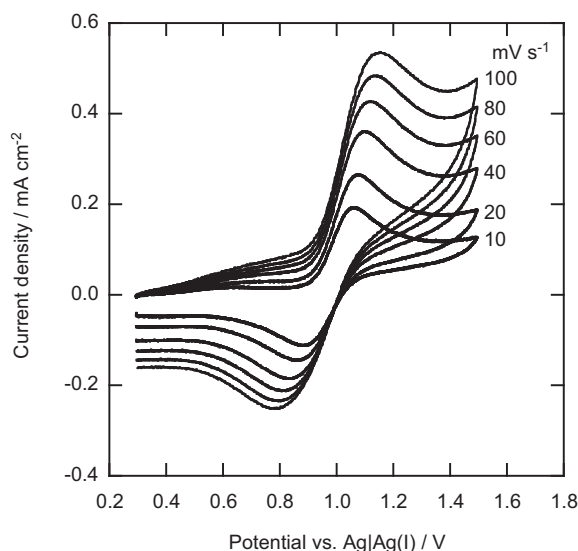


Fig. 2. Cyclic voltammograms of a Pt electrode in BMPTFSA containing 40 mM $[\text{Ni}(\text{bpy})_3]^{2+}$ at 25 °C. Scan rates: 10, 20, 40, 60, 80 and 100 mV s^{-1} .

transfer reaction at 25 °C. Consequently, it was verified that the electrode reaction was represented by eq. (1). The formal potential was calculated to be 0.95 V, which is corresponding to 1.37 V vs. Fc/Fc^+ . This formal potential is close to those reported in liquid SO_2 (1.325 V) [16] and acetonitrile (1.39 V) [19].

Chronoamperometry was carried out in order to determine the diffusion coefficients of $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$. Fig. 4 shows the Cottrell plots of a platinum electrode in BMPTFSA containing 20 mM $[\text{Ni}(\text{bpy})_3]^{2+}$ and $[\text{Ni}(\text{bpy})_3]^{3+}$ at various temperatures. It was confirmed that the current density, j , was proportional to the reciprocal square root of time, t , from the potential step. The diffusion coefficient of a species, D , can be calculated from the slope of the line according to Cottrell equation [20].

$$j(t) = \frac{nFD^{1/2}C}{\pi^{1/2}t^{1/2}} \quad (3)$$

where n is the number of electrons transferred in the electrode reaction, F is the Faraday constant and C is the bulk concentration of the species. The diffusion coefficients calculated

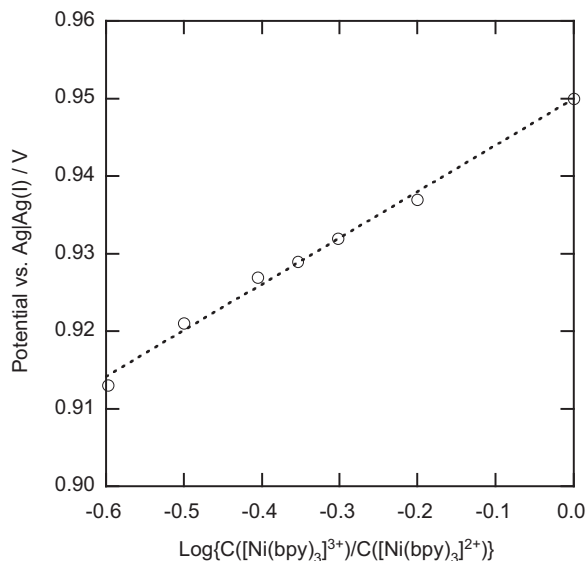


Fig. 3. Open circuit potentials of a Pt electrode during the intermittent potentiostatic oxidation of $[\text{Ni}(\text{bpy})_3]^{2+}$ to $[\text{Ni}(\text{bpy})_3]^{3+}$ in BMPTFSA at 25 °C.

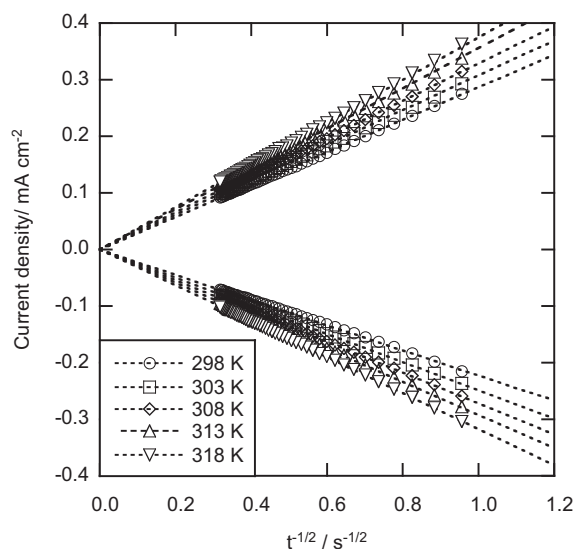


Fig. 4. Cottrell plots of a Pt electrode in BMPTFSA containing 20 mM $[\text{Ni}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ni}(\text{bpy})_3]^{3+}$. The potential was stepped to ± 300 mV from the equilibrium potential.

from eq. (3) at 25 °C are listed in Table 1 together with those of some other bpy complexes. The diffusion coefficient of $[\text{Ni}(\text{bpy})_3]^{2+}$ is close to those of $[\text{Fe}(\text{bpy})_3]^{2+}$ and $[\text{Ru}(\text{bpy})_3]^{2+}$. Since the sizes of these complexes are close to one another, the diffusion coefficients are approximately identical according to Stokes-Einstein relation. Similarly, the diffusion coefficient of $[\text{Ni}(\text{bpy})_3]^{3+}$ is close to those of $[\text{Fe}(\text{bpy})_3]^{3+}$ and $[\text{Ru}(\text{bpy})_3]^{3+}$. However, the diffusion coefficient of $[\text{Ni}(\text{bpy})_3]^{2+}$ is always larger than that of $[\text{Ni}(\text{bpy})_3]^{3+}$, although the size of $[\text{Ni}(\text{bpy})_3]^{2+}$ is close to that of $[\text{Ni}(\text{bpy})_3]^{3+}$. The similar tendency has been found for iron and ruthenium bpy complexes, indicating the diffusivity of a charged species in ionic liquids is affected by the coulombic interaction between the species and the ions of ionic liquids [2–4]. The ratio of the diffusion coefficients of trivalent to divalent species, D_{3+}/D_{2+} , for nickel bpy complexes is 0.60, which is close to those for iron and ruthenium bpy complexes in BMPTFSA, since the D_{3+}/D_{2+} is mainly determined by the anion of ionic liquid [3,4]. Fig. 5 shows the dependence of the diffusion coefficients of $[\text{Ni}(\text{bpy})_3]^{3+}$ and

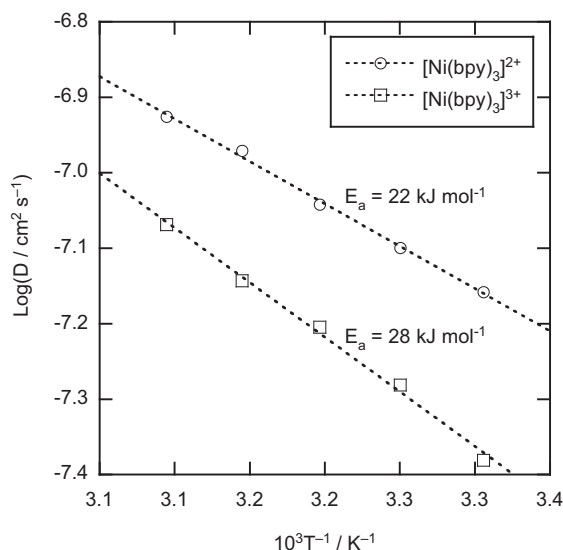
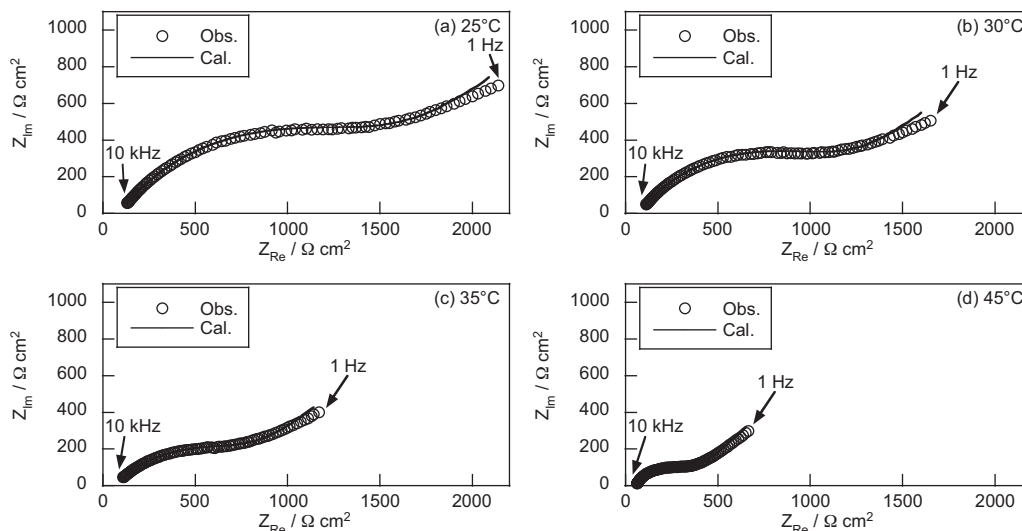


Fig. 5. Temperature dependence of the diffusion coefficients (D) of $[\text{Ni}(\text{bpy})_3]^{2+}$ and $[\text{Ni}(\text{bpy})_3]^{3+}$ in BMPTFSA.

Table 1

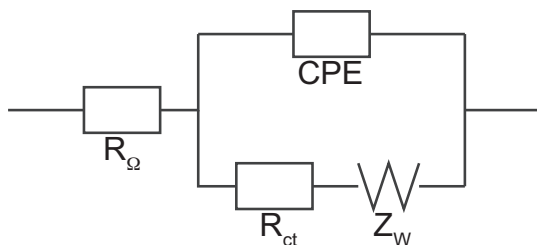
Diffusion coefficients of some bpy complexes in BMPTFSA at 25 °C.

Species	$10^8 D / \text{cm}^2 \text{ s}^{-1}$	$E_a(D) / \text{kJ mol}^{-1}$	$E_a(\eta) / \text{kJ mol}^{-1}$	D_{3+} / D_{2+}	Ref.
$[\text{Ni}(\text{bpy})_3]^{2+}$	7.0	22	25	0.60	This work
$[\text{Ni}(\text{bpy})_3]^{3+}$	4.2	28			
$[\text{Ru}(\text{bpy})_3]^{2+}$	7.3	23	25	0.63	3
$[\text{Ru}(\text{bpy})_3]^{3+}$	4.6	23			
$[\text{Fe}(\text{bpy})_3]^{2+}$	7.1	28	25	0.72	2
$[\text{Fe}(\text{bpy})_3]^{3+}$	5.1	29			

**Fig. 6.** Nyquist plots of a Pt electrode in BMPTFSA containing 20 mM $[\text{Ni}(\text{bpy})_3]^{2+}$ and 20 mM $[\text{Ni}(\text{bpy})_3]^{3+}$ at (a) 25, (b) 30, (c) 35 and (d) 45 °C. Frequency: 1 Hz – 10 kHz, Amplitude: 10 mV rms.

$[\text{Ni}(\text{bpy})_3]^{2+}$ on the absolute temperature, T . The activation energies of the diffusion coefficients of $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$ were 28 and 22 kJ mol^{-1} , respectively, which are close to that of viscosity of the ionic liquid, 25 kJ mol^{-1} , indicating the viscosity is still a major factor that determines the diffusivity of the species.

Fig. 6 shows the Nyquist plots of a platinum electrode in BMPTFSA containing 20 mM $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$ at various temperatures. The impedance measurements were conducted at the equilibrium potentials. The impedance data were analyzed by a Randles-type equivalent circuit using a constant phase element (CPE) instead of capacitor, as shown in Fig. 7. The fitting results are also shown with solid curves in Fig. 6. The diameter of vertically distorted semi-circle observed in the higher frequency region is corresponding to the charge transfer resistance, R_{ct} . It is obvious that R_{ct} decreased with elevating temperature, indicating the electrode reaction is facilitated with temperature. The standard rate constant, k^0 , can be calculated from R_{ct} according to the following equation.

**Fig. 7.** Equivalent circuit used for analysis of the impedance data.

$$k^0 = \frac{RT}{nF^2 R_{\text{ct}} C} \quad (4)$$

where C is the bulk concentration of $[\text{Ni}(\text{bpy})_3]^{3+}$ and $[\text{Ni}(\text{bpy})_3]^{2+}$, which are the same in this case and R is the gas constant. Fig. 8 shows the Arrhenius plots of k^0 in the ionic liquid. The logarithm of k^0 was linearly dependent on the reciprocal of temperature. The activation energy for k^0 , $E_a(k^0)$, was calculated to be $67 \pm 6 \text{ kJ mol}^{-1}$ from the slope of the regression line. Table 2 summarizes the rate constants of $[\text{M}(\text{bpy})_3]^{3+/2+}$ ($\text{M} = \text{Ni}, \text{Ru}$ and Fe) and their activation

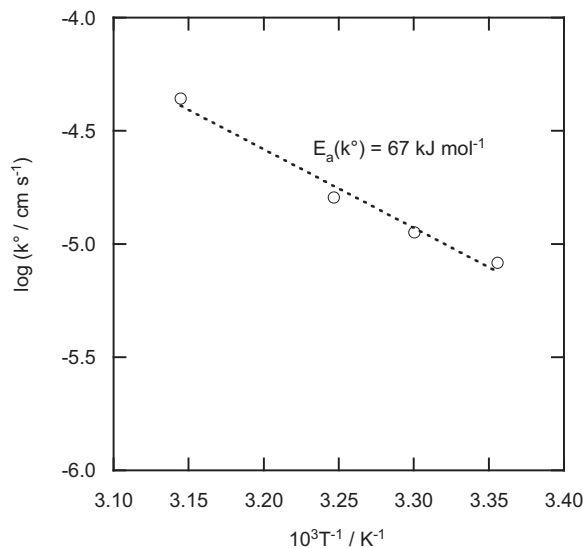
**Fig. 8.** Temperature dependence of the rate constant for $[\text{Ni}(\text{bpy})_3]^{3+}/[\text{Ni}(\text{bpy})_3]^{2+}$ couple in BMPTFSA.

Table 2
Rate constants (k^0) of $[\text{M}(\text{bpy})_3]^{3+/2+}$ (M = Ni, Ru and Fe) and their activation energies, $E_a(k^0)$, in BMPTFSA at 25 °C. The activation energies for the viscosity, $E_a(\eta)$, are also listed.

Redox couple	$k^0/\text{cm s}^{-1}$	$E_a(k^0)/\text{kJ mol}^{-1}$	$E_a(\eta)/\text{kJ mol}^{-1}$	Ref.
$[\text{Ni}(\text{bpy})_3]^{3+/2+}$	$(8.3 \pm 0.1) \times 10^{-6}$	67 ± 6	25	This work
$[\text{Ru}(\text{bpy})_3]^{3+/2+}$	$(4.5 \pm 0.4) \times 10^{-4}$	37	25	3
$[\text{Fe}(\text{bpy})_3]^{3+/2+}$	$(9.0 \pm 0.5) \times 10^{-4}$	24	25	2

energies in BMPTFSA at 25 °C. The rate constant for $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ is smaller by two orders of magnitude than those of $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ and $[\text{Fe}(\text{bpy})_3]^{3+/2+}$ probably due to the difference in the electron configurations. The center metal in each complex is octahedrally coordinated by nitrogen atoms of bpy ligands so that the d orbital is split into two energy levels, e_g (σ^*d) and t_{2g} (πd). The former is corresponding to the anti-bonding and the latter to the bonding molecular orbital. In case of $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ and $[\text{Fe}(\text{bpy})_3]^{3+/2+}$, the electron transfer occurs between $(t_{2g})^5$ and $(t_{2g})^6$, leading to negligible change in the bond length between the center metal and the nitrogen atoms of ligands. On the other hand, the electron transfer for $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ involves the change in the electron configuration between $(e_g)^1(t_{2g})^6$ and $(e_g)^2(t_{2g})^6$, resulting in a significant change in the bond length between the center metal and the nitrogen atoms of ligands since the anti-bonding molecular orbitals are occupied. The similar tendency has been also reported for electron exchange rate in homogeneous systems [21]. Thus, the slow kinetics for $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ is considered closely related to the inner component of the reorganization energy.

The rate constant for adiabatic reaction can be represented by the product of Kramer's transmission coefficient, κ_T , and the rate constant based on transition state theory, k_{TST} [5].

$$k^0 = \kappa_T k_{\text{TST}} = A \left(\frac{\lambda}{RT} \right)^{1/2} \tau_L^{-1} \exp \left(-\frac{\Delta^\ddagger G}{RT} \right) \quad (5)$$

where A is a constant, λ is the reorganization energy, τ_L is the longitudinal relaxation time and $\Delta^\ddagger G$ is the Gibbs energy of activation. It has been known that τ_L is approximately proportional to the viscosity of medium, η [20]. Thus, the k^0 is expected to be proportional to the following exponential term.

$$k^0 \propto \exp \left\{ -\frac{1}{RT} (E_a(\eta) + \Delta^\ddagger G) \right\} \quad (6)$$

where $E_a(\eta)$ is the activation energy for the viscosity of medium. Therefore, the apparent activation energy of the rate constant is expected to consist of the contributions of both $E_a(\eta)$ and $\Delta^\ddagger G$. Since $E_a(\eta)$ in BMPTFSA is 25 kJ mol⁻¹ regardless of the solute as listed in Table 2, the difference between $E_a(k^0)$ and $E_a(\eta)$ is considered corresponding to the contribution of $\Delta^\ddagger G$. The differences between $E_a(k^0)$ and $E_a(\eta)$ for $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ are larger than that for $[\text{Fe}(\text{bpy})_3]^{3+/2+}$, indicating the contribution of $\Delta^\ddagger G$ to the activation energy is significant in $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+/2+}$. At the equilibrium potential, $\Delta^\ddagger G$ can be assumed to be a quarter of the reorganization energy, which can be divided into the inner and outer contributions, λ_{Inner} and λ_{Outer} , respectively.

$$\Delta^\ddagger G = \frac{\lambda}{4} = \frac{1}{4} (\lambda_{\text{Inner}} + \lambda_{\text{Outer}}) \quad (7)$$

In case of $[\text{Fe}(\text{bpy})_3]^{3+/2+}$, the contribution of $\Delta^\ddagger G$ to $E_a(k^0)$ is very small, suggesting λ_{Outer} is considered very small. Since λ_{Outer} is considered related to the charge densities of the complexes, λ_{Outer} for $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ and $[\text{Ru}(\text{bpy})_3]^{3+/2+}$ is also expected to be very small since the sizes of all these complexes can be regarded as the same. Therefore, the differences between $E_a(k^0)$ and $E_a(\eta)$ are considered mostly reflecting λ_{Inner} . The large λ_{Inner} in $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ can be ascribed to displacement of the bond lengths between the

center metal and the ligands due to participation of electrons in anti-bonding molecular orbitals, as described above.

4. Conclusions

The electrode reaction of $[\text{Ni}(\text{bpy})_3]^{3+/2+}$ in BMPTFSA was found to be sluggish mainly because the inner component of reorganization energy is large due to participation of electrons in anti-bonding molecular orbitals during the redox reaction. The inner component of reorganization energy could be evaluated from the apparent activation energies for the diffusion coefficients and the rate constant, which was estimated by AC impedance spectroscopy. Thus, the investigation of the redox reactions of metal complexes in ionic liquids using AC impedance spectroscopy may provide useful information of the electrode kinetics, which is often too facile to be measured in conventional electrolytes.

Acknowledgements

Part of this study was financially supported by MEXT-Supported Program for the Strategic Research Foundation at Private Universities, 2012–2016.

References

- [1] H. Ohno (Ed.), *Electrochemical Aspects of Ionic Liquids*, 2nd Ed., John Wiley & Sons, Inc, 2011.
- [2] N. Tachikawa, Y. Katayama, T. Miura, Electrode Kinetics of Some Iron Complexes in an Imide-Type Room-Temperature Ionic Liquid, *J. Electrochem. Soc.* 154 (2007) F211–F216.
- [3] Y. Toshimitsu, Y. Katayama, T. Miura, Electrode reactions of ruthenium–bipyridine complex in amide-type ionic liquids, *Electrochim. Acta* 82 (2012) 43–47.
- [4] Y. Katayama, Y. Toshimitsu, T. Miura, Electrode Kinetics of Tris(2,2'-bipyridine)ruthenium Complexes in 1-Ethyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid, *J. Electrochem. Soc.* 160 (2013) H219–H228.
- [5] W.R. Fawcett, *Liquids, Solutions, and Interfaces from classical macroscopic description to modern microscopic details*, Oxford University Press, Oxford, New York, 2004.
- [6] Y. Katayama, I. Konishiike, T. Miura, T. Kishi, Redox reaction in 1-ethyl-3-methylimidazolium-iron chlorides molten salt system for battery application, *J. Power Sources* 109 (2002) 327–332.
- [7] M. Yamagata, N. Tachikawa, Y. Katayama, T. Miura, Electrochemical behavior of iron(II) species in a hydrophobic room-temperature molten salt, *Electrochemistry* 73 (2005) 564–566.
- [8] M. Yamagata, Y. Katayama, T. Miura, Electrochemical Behavior of Samarium, Europium, and Ytterbium in Hydrophobic Room-Temperature Molten Salt Systems, *J. Electrochem. Soc.* 153 (2006) E5–E9.
- [9] M. Yamagata, N. Tachikawa, Y. Katayama, T. Miura, Electrochemical Behavior of Several Iron Complexes in Hydrophobic Room-temperature Ionic Liquids, *Electrochim. Acta* 52 (2007) 3317–3322.
- [10] J.-H. Kim, K.J. Kim, M.-S. Park, N.J. Lee, U. Hwang, H. Kim, Y.-J. Kim, Development of metal-based electrodes for non-aqueous redox flow batteries, *Electrochemistry Communications* 13 (2011) 997–1000.
- [11] M.H. Chakrabarti, R.A.W. Dryfe, E.P.L. Roberts, Evaluation of electrolytes for redox flow battery applications, *Electrochim. Acta* 52 (2007) 2189–2195.
- [12] Y. Katayama, H. Onodera, M. Yamagata, T. Miura, Electrochemical Reduction of Oxygen in Some Hydrophobic Room-Temperature Molten Salt Systems, *J. Electrochem. Soc.* 151 (2004) A59–A63.
- [13] Y.-L. Zhu, Y. Katayama, T. Miura, Electrochemical Behavior of Ni(II)/Ni in a Hydrophobic Amide-type Room-temperature Ionic Liquid, *Electrochim. Acta* 54 (2009) 7502–7506.
- [14] Y. Yamato, Y. Katayama, T. Miura, Effects of the Interaction between Ionic Liquids and Redox Couples on Their Reaction Entropies, *J. Electrochem. Soc.* 160 (2013) H309–H314.

- [15] R.R. Ruminski, J.D. Petersen, Tris(2,2'-bipyrimidine)M (M=Fe(II), Co(II), Ni(II)) perchlorate complexes. Spectroscopic properties for precursor complexes in the preparation of polymetallic systems, *Inorg. Chim. Acta* 97 (1985) 129–134.
- [16] J.B. Chlistunoff, A.J. Bard, Electrochemistry in liquid sulfur dioxide. 11. Oxidation of tris(2,2'-bipyridine)nickel(2+) and spectroscopy and isolation of products, *Inorg. Chem* 31 (1992) 4582–4587.
- [17] P.N. Bartlett, V. Eastwick-Field, A reinvestigation of the electrochemistry of $[\text{Ni}^{(\text{II})}(\text{bpy})_3(\text{ClO}_4)_2]$ in acetonitrile using rotating disc and rotating ring-disc electrodes, *Electrochim. Acta* 38 (1993) 2515–2523.
- [18] B.J. Henne, D.E. Bartak, Metal-vapor synthesis and electrochemistry of bis(bipyridyl)nickel(0), *Inorg. Chem.* 23 (1984) 369–373.
- [19] R. Prasad, D.B. Scaife, Electro-oxidation and electro-reduction of some iron (II), cobalt(II) and nickel(II) polypyridyl complexes in acetonitrile, *J. Electroanal. Chem. Interfacial Electrochem* 84 (1977) 373–386.
- [20] A.J. Bard, L.R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, 2nd Ed., John Wiley & Sons, New York, 2001.
- [21] D.H. Macartney, N. Sutin, Electron-exchange rates of polypyridine complexes: electron-transfer reactions involving the tris(polypyridine)nickel(II/III) couple in acidic aqueous media, *Inorg. Chem.* 22 (1983) 3530–3534.